

Discovery of Photocatalysts for Hydrogen Production

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Objectives

- To design and construct tools for the high throughput screening of the properties of photocatalysts relevant to the photoelectrochemical generation of hydrogen.
- To use the high throughput screening tools to identify materials with the appropriate energetics for water splitting.
- To use the industrially relevant laser pyrolysis materials production capability of our partner, NanoGram Corp., to produce commercial scale quantities of photocatalysts.
- Demonstrate that materials issues that are a hindrance to the commercialization of photoelectrochemical water splitting can be addressed through a materials discovery process.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- M. Materials Durability
- N. Materials and Systems Engineering
- O. Photoelectrochemical Efficiency

Approach

- Develop tools for the high throughput analysis of material properties relevant to photoelectrochemical hydrogen generation.
- Work with existing nanoparticulate powder manufacturer to test materials with existing technology to produce kg/hr scale quantities.
- Identify candidate materials for further study via high throughput screening.

Accomplishments

- Constructed Solar Simulator.
- Designed and constructed 25-cell photolysis analysis module.

- Acquired diffuse reflectance instrument employing Ocean Optics Spectrometer.
- Initiated evaluation of NanoGram NPMTM produced nanoparticulate titania.

Future Directions

- Modify stable metal oxide semiconductors to shift bandgap to increase utilization of the solar spectrum and increase solar to hydrogen efficiencies.
- Complete 25-cell module for electrochemical analysis of materials to provide band edge energy and photoaction spectrum analysis.
- Incorporate hydrogen sensor technology developed for fuel cell safety applications into analysis modules for direct hydrogen determination.
- Increase level of collaboration between other DOE funded laboratories via establishment of mutual database.

Introduction

The process whereby semiconductor materials absorb light and convert that light to electricity has been known for some time and is the cornerstone of the photovoltaic (PV) industry. As an alternative to generating electricity, the electron/hole pair generated by the absorption of light by a semiconductor could be used to facilitate a chemical transformation, thereby storing the energy for later use. This is the basis for the photoelectrochemical (PEC) generation of hydrogen from sunlight, water and a semiconductor-based photocatalyst. In this process, electrons generated by the absorption of light are used to reduce water, generating hydrogen, and the holes are used to oxidize water, generating oxygen. The hydrogen produced could then be used as a fuel in either electrolytic or combustion processes. It is more efficient to generate hydrogen using PEC directly than to use a PV array to feed an electrolyzer.

The key materials requirements for efficient PEC hydrogen production are: A) a semiconductor with a bandgap relevant to the solar spectrum so as to maximize solar utilization, B) band edge energies relevant to the reduction and oxidation potentials of water to minimize energy mismatch, C) fast interfacial electron transport to minimize recombination and D) stability in the presence of an aqueous electrolyte. The key technical barriers to the implementation of PEC hydrogen production relate to the fact that materials that satisfy all of these requirements, simultaneously, have not been found.

This is not due to a conflict with these requirements and known laws of physics (there are none), but rather reflects the immature stage of this technology. In the earliest work on this technology, semiconductor materials developed for the PV industry were analyzed and found to be unsuitable due to their poor stability in aqueous electrolytes. Current work is under way with respect to the identification of materials specifically for the purpose of photoelectrochemical generation of hydrogen.

Approach

The use of high throughput techniques to speed the discovery process has been in place for a number of years; pharmaceutical companies were the first to invest heavily in the combinatorial synthesis and high throughput analysis concept. The key to the concept is to test as many samples as possible as quickly as possible for a specific property rather than to do a complete characterization on a specific material or class of materials. In this manner, candidates for further study can be culled from very large sample sets. In our approach to develop tools for the high throughput screening of materials for properties relevant to PEC hydrogen production, we have designed and built a 25-cell module to analyze the photolysis products generated upon illumination of samples with a simulated solar spectrum. The basic design incorporates a vacuum sealed sample module with a pressure transducer to monitor the pressure as a function of photolysis time, see Figure 1. The pressure transducer data is computer

monitored, and at set pressure intervals, a Gillson sample handler (top right of Figure 1) that has been modified is triggered to sample the head space gas and feed it to a gas chromatograph for analysis. The vacuum seal component of this design ensures that each cell is isolated, and the quick release and seal capabilities make loading quick and easy.

In the Hydrogen, Fuel Cells and Infrastructure Technologies Program (HFCIT) Multi-Year Program Plan, the need to have processes for the commercially relevant production of PEC materials is identified. Part of the sample lots that we are investigating are produced by NanoGram Corp. using their nanoparticle manufacturing technology, NPMTM. NanoGram has the process technology to produce these materials at rates of kilograms per hour and higher should a demand for these materials arise.

Results

To date, the key results involve the design and construction of the 25-cell photolysis analysis module, which we have now fully engaged in the initial screening of sample sets of nanoparticulate titania provided by our partner, NanoGram Corp. The photolysis setup delivers a photon flux on the order of 80 mW/cm^2 to the sample cells as determined by actinometry. An interesting observation is that the pressure transducer response factor is slowly changing. This was noticed during

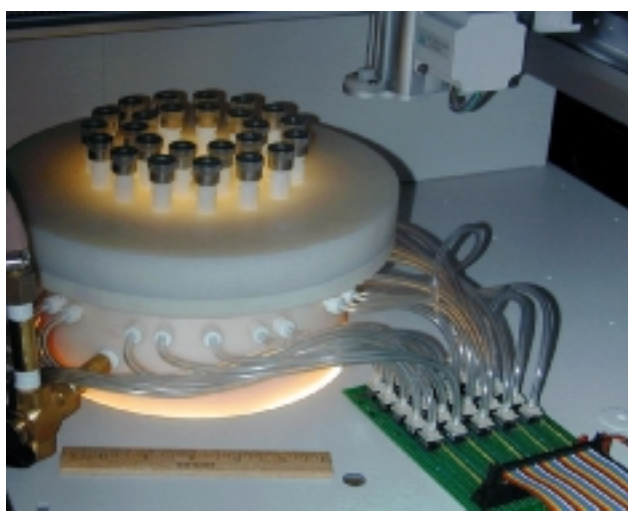


Figure 1. Picture of 25-Cell Photolysis Analysis Module

the course of a routine pressure testing in which we had initially observed very a very narrow distribution of pressure responses; however, after a number of experiments, the distribution of response factors appeared to increase, see Figure 2. As such, we now routinely collect a calibration curve for the pressure transducers. As shown in Figure 3, while the response factors of the various pressure transducers does vary considerably, the response of any given transducer is very linear over pressure ranges encountered during the normal course of operation.

A sample data set collected during the course of a photolysis experiment is shown in Figure 4. Contained with the 25 sample cells are 6 TiO_2 samples in triplicate, one Niobate in triplicate and four blanks containing a similar particulate that is known to be inactive. The data set has been corrected for the photon flux for each specific cell and for the pressure transducer response. From this

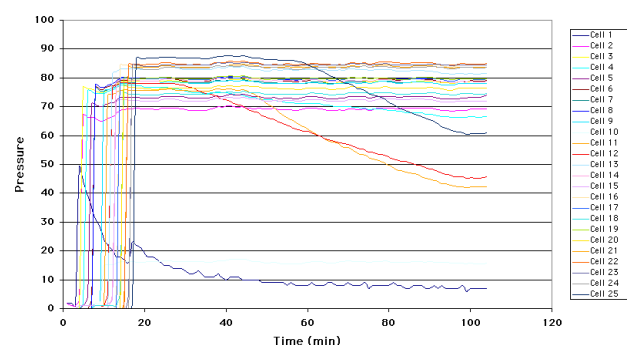


Figure 2. Leak Test Results Indicating Range of Pressure Transducer Response Factor

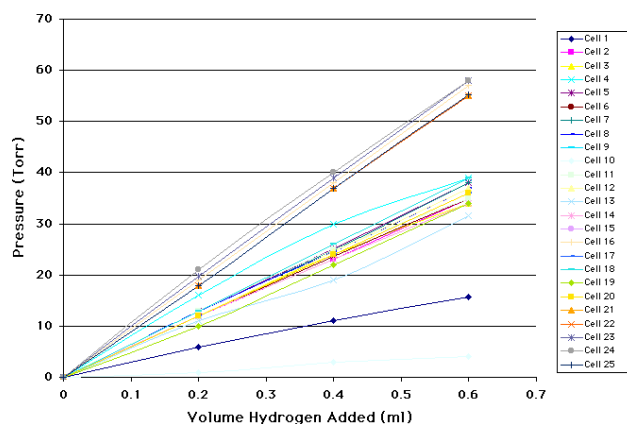


Figure 3. Results of Calibration of Pressure Transducer Response Factor

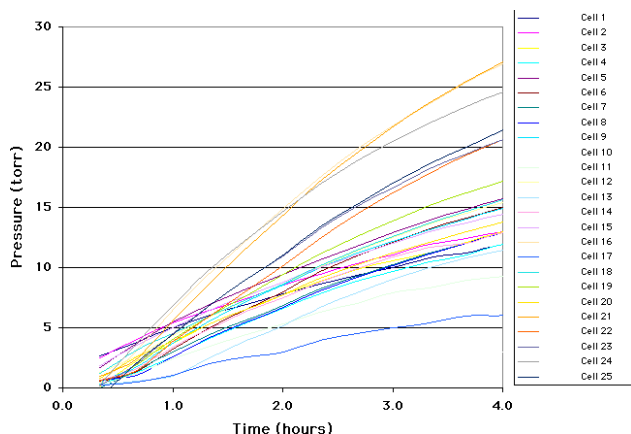


Figure 4. Time Versus Pressure Results

experiment, the niobate sample resulted in the best efficiency and the highest pressure versus time plots, followed by an oxygen-deficient phase of titania which does extend the absorption spectrum into the visible. The niobate, while still exhibiting efficiencies of less than 1%, is a material that we will be investigating further in various modified forms. To date, we have received over 50 different samples from NanoGram, with the majority of them being titania samples prepared over a significant range of particulate sizes, see Table 1.

In our initial screen of the TiO_2 samples, a platinum catalyst was deposited onto the particle sets via the photoreduction of a platinum salt. Samples have also been prepared using chemical reduction of impregnated platinum salts; however, these to date

Table 1. Partial TiO_2 Sample List Indicating Particle Size and Surface Area

Sample	median diameter, μm	Surface area, m^2/gm
TDX-25	0.11	20.9
TDX-33	0.10	20.1
TDX-30	0.08	22.8
TDX-101	0.08	27.9
TDX-37	0.07	26.2
TDX-51	0.07	25.3
DIM76	0.07	38.0
TDX-50A	0.06	29.4
TDX-55	0.06	29.0
TDX-110	0.06	33.6
TDX-24	0.05	32.8
DIM57	0.04	52.5
DIM113	≤ 0.03	56.0
DIM82	≤ 0.03	55.6

have not been screened. In the titania series prepared with the photoreduced platinum catalyst, we see no statistical variation in the efficiency of hydrogen generation as a function of particle size, and in all cases efficiencies were in the range of 0.1% solar photons to hydrogen. Interestingly, there does appear to be a trend developing with respect to the hydration of the titania. These results are very premature, and considering the overall rather disappointing performance of these materials to date, it is doubtful that time will be spent analyzing them further with the platinum catalyst. We are currently evaluating these materials with other catalysts. We are also currently expanding the materials we are looking at to include some niobate structures. These materials have shown evidence of water splitting in the past and the extension of their absorbance spectra into the visible relative to the titania samples, see Figure 5.

Conclusions

Our initial results, while far from complete or conclusive, indicate that the nanoparticulate titania samples provided by NanoGram Corp. exhibit very poor efficiencies for the conversion of photons of solar relevance to hydrogen. In no case were conversion efficiencies greater than 0.3% observed in any of the titania samples. This clearly indicates that we need to expand the composition of materials being explored. With the relocation of one of NanoGram Corporation's laser pyrolysis instruments to the SRI campus, we will be able to facilitate this expansion of material candidates considerably.

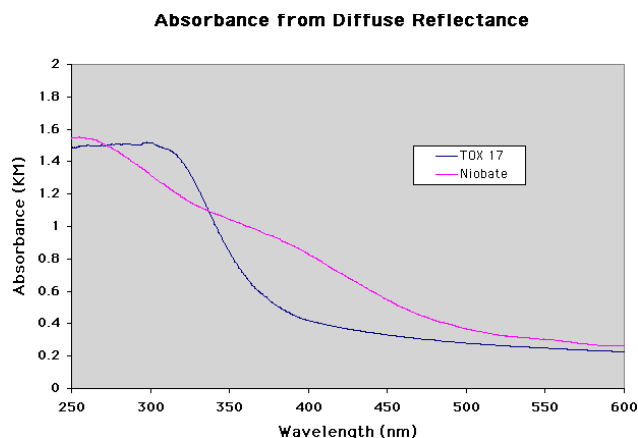


Figure 5. Absorbance spectra generated from diffuse reflectance data for a titania, TOX 17, and a niobate semiconductor sample.

FY 2003 Publications/Presentations

1. Brent MacQueen, "Photoelectrochemical Hydrogen Production", Invited Lecture, Hydrogen Workshop of the Global Climate Energy Project, March 2003, Stanford University, Palo Alto CA.